Yet More Gibbs!

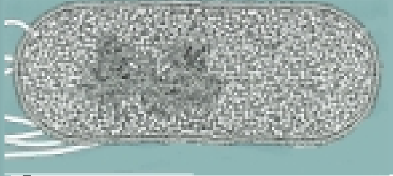
1) Exam Results

1) A brief discussion of partial derivatives

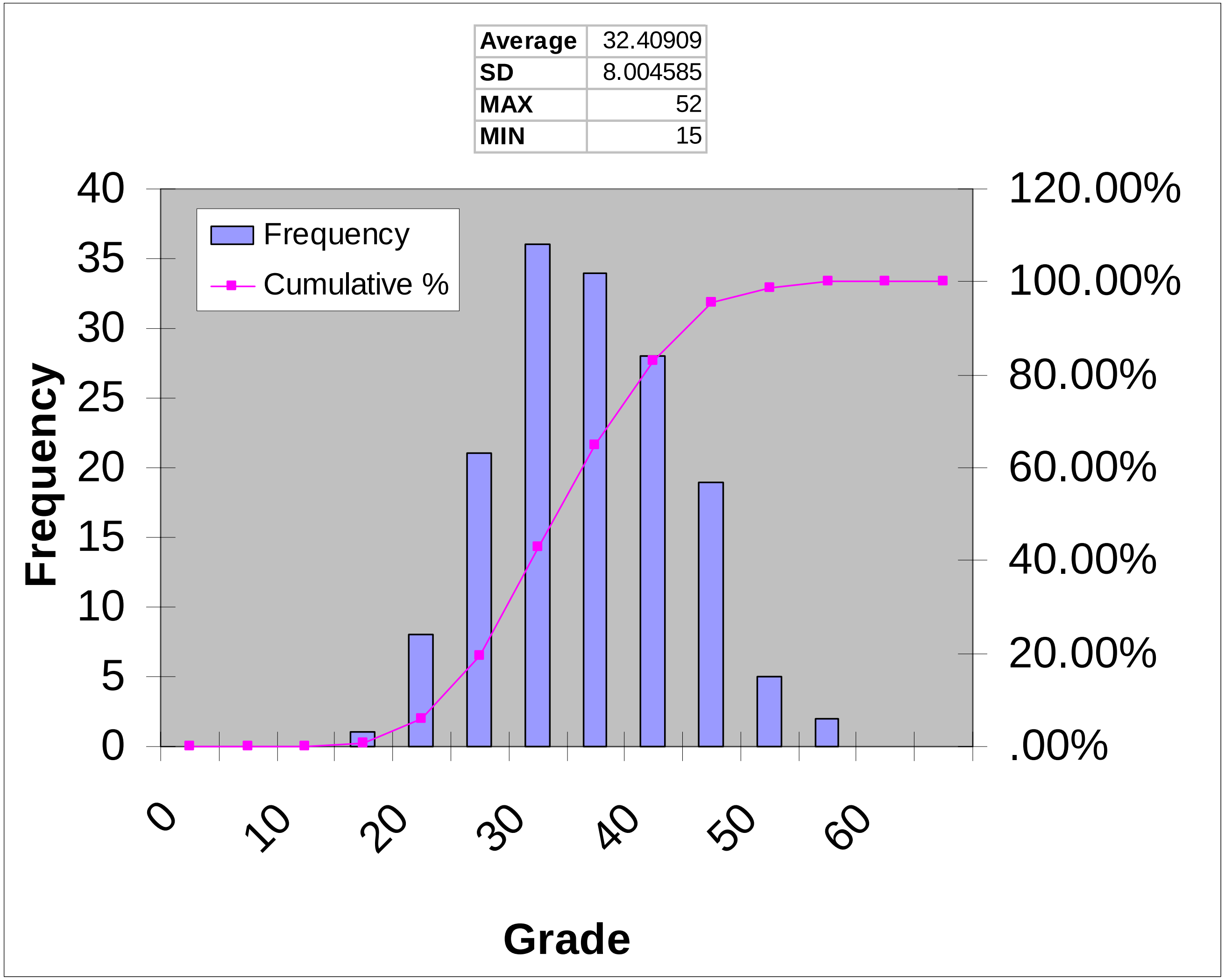
2) Equilibrium and Life

3) Free energy and Equilibrium

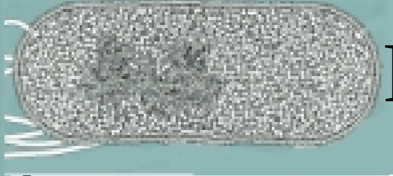
Reading: Last half of Chapter 3, pp. 84-114, and Chapter 4, pp.123-134



Exam Results



Average	32.40909
SD	8.004585
MAX	52
MIN	15



Pressure Dependence: Example

For the pressure dependence we hold T constant:

$$dG \leq VdP - SdT = VdP$$

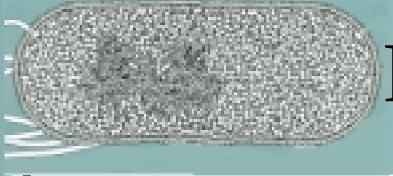
Thus,

$$\Delta G = \int_{1}^{2} VdP$$

And for an ideal gas:

$$\Delta G = \int_{1}^{2} VdP = \int_{P_1}^{P_2} \frac{nRT}{P} dP = nRT \ln\left(\frac{P_2}{P_1}\right)$$

Does the free energy behave as expected?
Note that unlike in the puzzle, P is not constant!



Pressure Dependence: Example

But is ΔG a criterion for spontaneity of the expansion of an ideal gas?

$$\Delta G = \int_{1}^{2} V dP = \int_{P_1}^{P_2} \frac{nRT}{P} dP = nRT \ln\left(\frac{P_2}{P_1}\right)$$

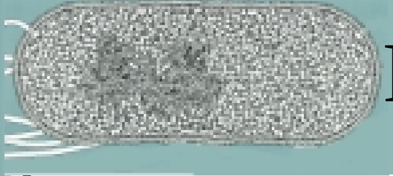
The pressure changed! So we can’t use:

$$\Delta G < 0$$

as a criterion. We must use the full form!

Assuming an isothermal expansion:

$$dG \leq VdP - SdT = VdP$$



Partial Derivatives 1

Equations like

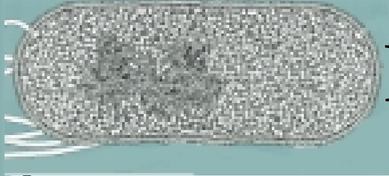
$$dG = VdP - SdT$$

that we have derived for a reversible process, can be rewritten like:

$$dG = \left(\frac{\partial G}{\partial P}\right)_T dP + \left(\frac{\partial G}{\partial T}\right)_P dT$$

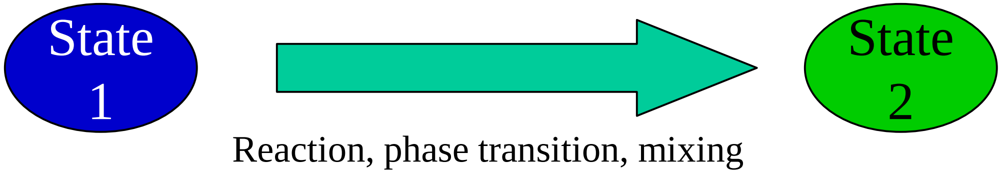
which assumes that these equations are perfect differentials. This one is , since it is for a state function.
That is,

$$\left(\frac{\partial G}{\partial P}\right)_T = V, \left(\frac{\partial G}{\partial T}\right)_P = -S$$



Partial Derivatives 2

So if we have a process we're interested say:



State 1

State 2

Reaction, phase transition, mixing

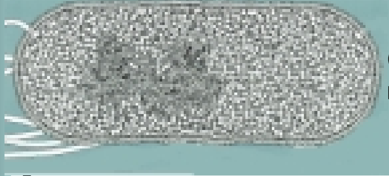
$$\left(\frac{\partial G_1}{\partial P}\right)_T = V_1, \left(\frac{\partial G_1}{\partial T}\right)_P = -S_1 \qquad \left(\frac{\partial G_2}{\partial P}\right)_T = V_2, \left(\frac{\partial G_2}{\partial T}\right)_P = -S_2$$

Which implies:

$$\left(\frac{\partial \Delta G}{\partial P}\right) = \left(\frac{\partial G_2}{\partial P}\right) - \left(\frac{\partial G_1}{\partial P}\right) = \left(\frac{\partial (G_2 - G_1)}{\partial P}\right) = V_2 - V_1 = \Delta V$$

So,

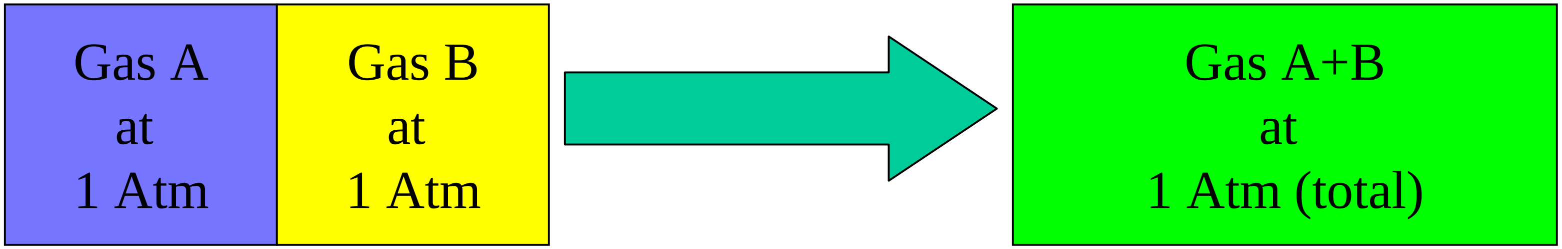
$$\Delta G(P_2) - \Delta G(P_1) = \int \Delta V dP$$



Some examples

Just to make sure we’re all on the same page let’s work some examples.

Consider the isobaric, isothermal mixing of two gases:



Gas A
at
1 Atm

Gas B
at
1 Atm

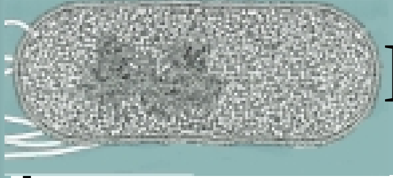
Gas A+B
at
1 Atm (total)

$$\Delta G_{mixing} = \Delta G_{\text{expansion of A}} + \Delta G_{\text{expansion of B}}$$

$$\Delta G_{mixing} = n_A RT \ln\left(\frac{P_{2,A}}{1atm}\right) + n_B RT \ln\left(\frac{P_{2,B}}{1atm}\right)$$

Is this reaction spontaneous?

Well, both $P_{2,A}$ and $P_{2,A}$ are less than 1 atm…so yes, this process is spontaneous.



Example 2

$$\mathrm{H_2O\ (l)} \overset{100\ ^\circ\mathrm{C}}{\rightleftharpoons} \mathrm{H_2O\ (g)}$$

What is the free energy change?

Well, this is at **constant T and P**. Its **reversible**. So,

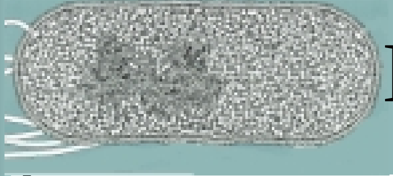
$$\Delta G^\circ_{vap} = 0 = \Delta H^\circ_{vap} - T\ \Delta S^\circ_{vap}$$

Note that this implies:

$$\frac{\Delta H^\circ_{vap}}{T} = \Delta S^\circ_{vap}$$

Which we’ve seen before.

What is ΔG at different T and P? Can it be zero?



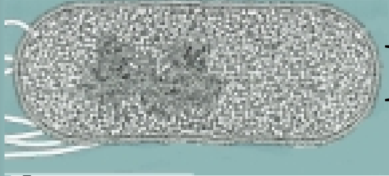
Example 3

A friend claims to have discovered a catalyst that allows benzene, a valuable hydrocarbon product, to form by passing H_2(g) over graphite at standard temperature and pressure. Should you buy stock in his company?

Data:

	ΔH kJ/mol	S J/K mol	ΔG kJ/mol
C_6H_6 (g)	49.04	173.26	124.35
C_6H_6 (l)	82.93	269.20	129.66
H_2 (g)	0.00	130.684	0.0
C_6(graphite)	0.00	5.740	0.0

a) Buy Stock
b) Don’t buy stock
c) Can’t tell.



Example 3

a) Buy Stock
b) Don’t buy stock
c) Can’t tell.

Well,

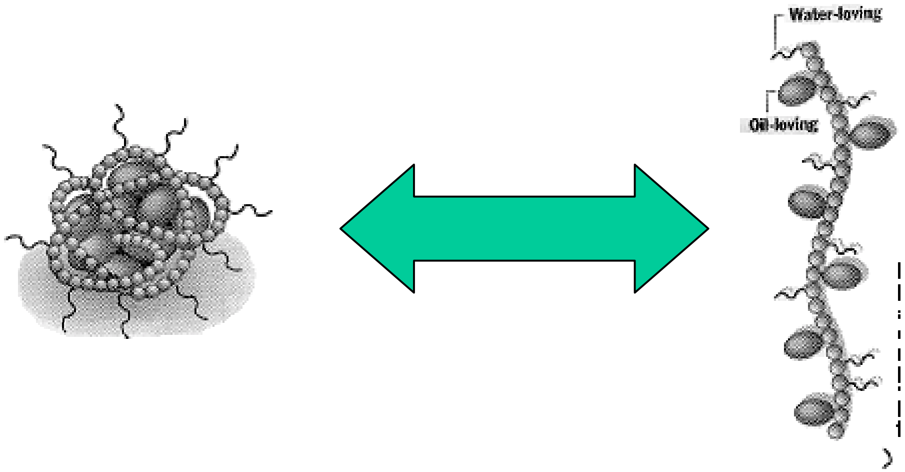
$$\Delta G_{rxn} = \Delta G_{(g,l)} - 0.0 - 0.0 > 0$$

The process is non-spontaneous. The catalyst won’t help!

If it were spontaneous, could the catalyst help?

What restrictions might be lifted to get this reaction to go spontaneously?

Example 4: Protein Denaturation



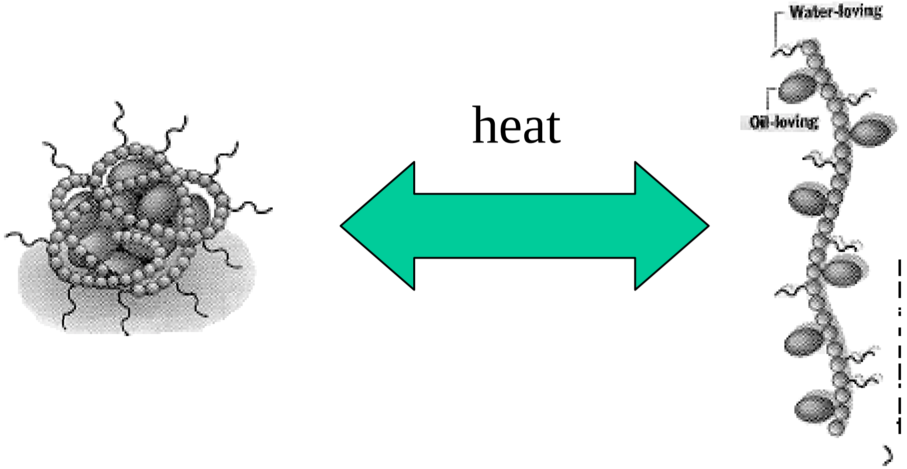
Proteins have a native state. (Really, they tend to have a tight cluster of native states.)

Denaturation occurs when heat or denaturants such as guanidine, urea or detergent are added to solution. Also, the pH can affect folding.

When performing a denaturation process non-covalent interactions are broken.

Ionic, van der-Waals, dipolar, hydrogen bonding, etc.
Solvent is reorganized.

Example 4: Protein Denaturation

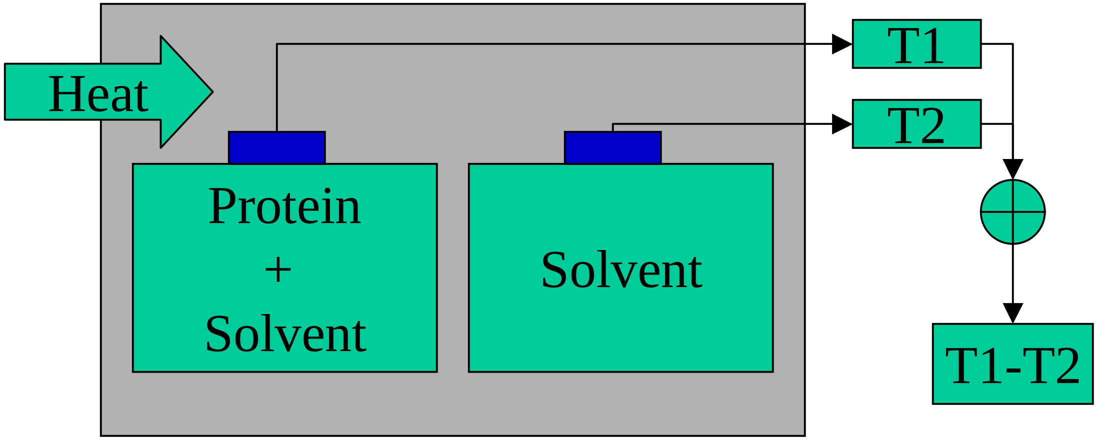


Let’s consider denaturation with heat. We can determine a great deal about the nature of the protein from such a consideration.

The experimental technique we use for measuring thermodynamic changes here is the differential scanning calorimeter.

Basic experiment: Add heat to sample, measure its temperature change.

Example 4: Protein Denaturation


Heat
Protein
+
Solvent
Solvent
T1
T2
T1-T2

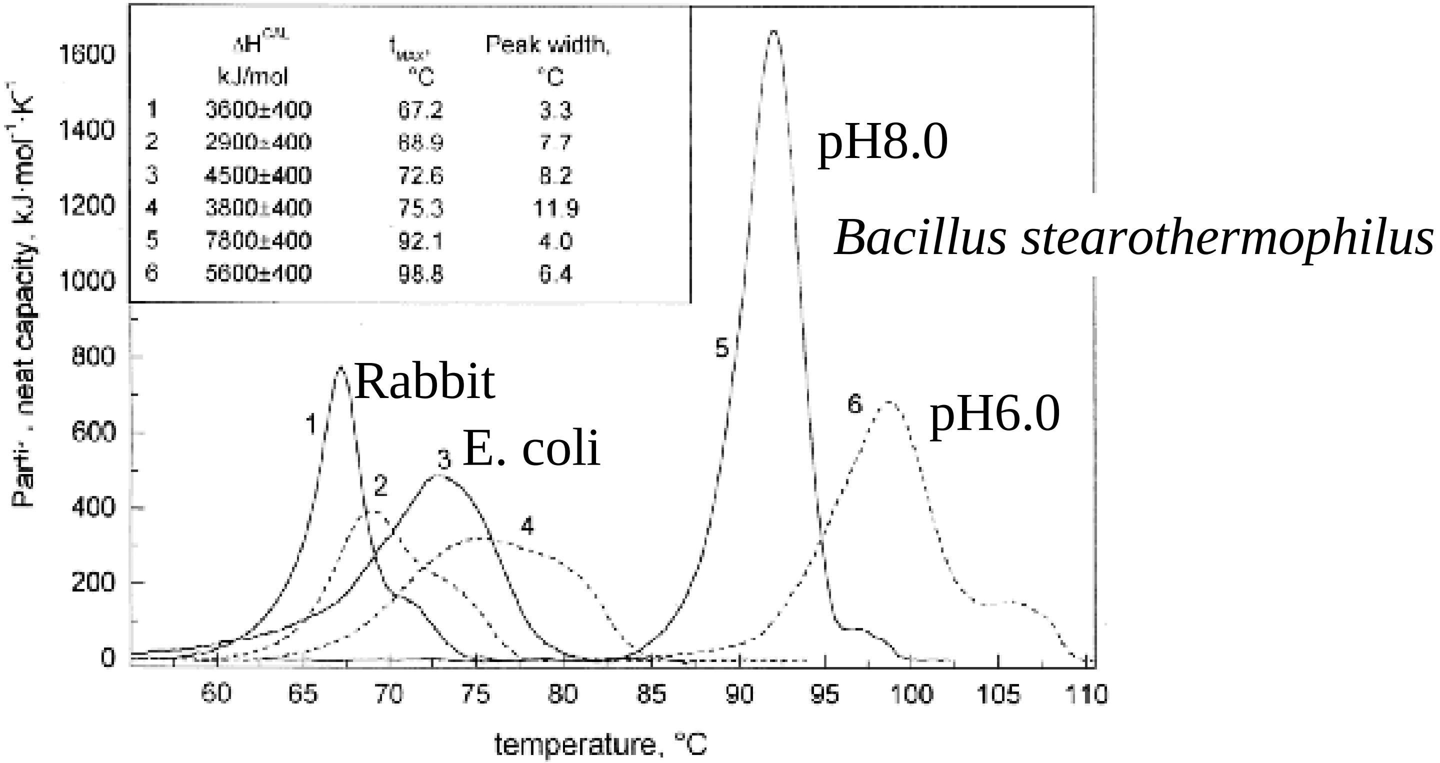
In differential scanning calorimetry you have two samples:

- Your material of interest
- Control

You put in an amount of heat to raise the temperature of the control at a constant rate, then measure the rate of change in temperature of the other sample as a function of the input heat.

This is a measure of the heat capacity!

Example 3



	ΔH^{cal}, kJ/mol	t_{max}, °C	Peak width, °C
1	3600±400	67.2	3.3
2	2900±400	68.9	7.7
3	4500±400	72.6	8.2
4	3800±400	75.3	11.9
5	7800±400	92.1	4.0
6	5600±400	98.8	6.4

Fig. 1. Differential scanning thermograms of GAPDHs isolated from rabbit muscle (1,2), *E. coli* (3,4) and *B. stearothermophilus* (5,6). Holoenzymes were used, the protein concentrations being 1 mg/ml (7.1 μM calculated per tetramer). The measurements were performed in 100 mM KH_2PO_4–KOH buffer containing 1 mM NAD^+ at pH 8.0 (samples 1, 3 and 5) and pH 6.0 (samples 2, 4 and 6). Heating rate, 1°C/min. The widths of the peaks were measured at half-heights of the peaks.

Data for glyceraldehyde-3-phosphate dehydrogenase.

Is the protein more stable at pH 8 or 6? Why is B. stear. more stable?

Example 3

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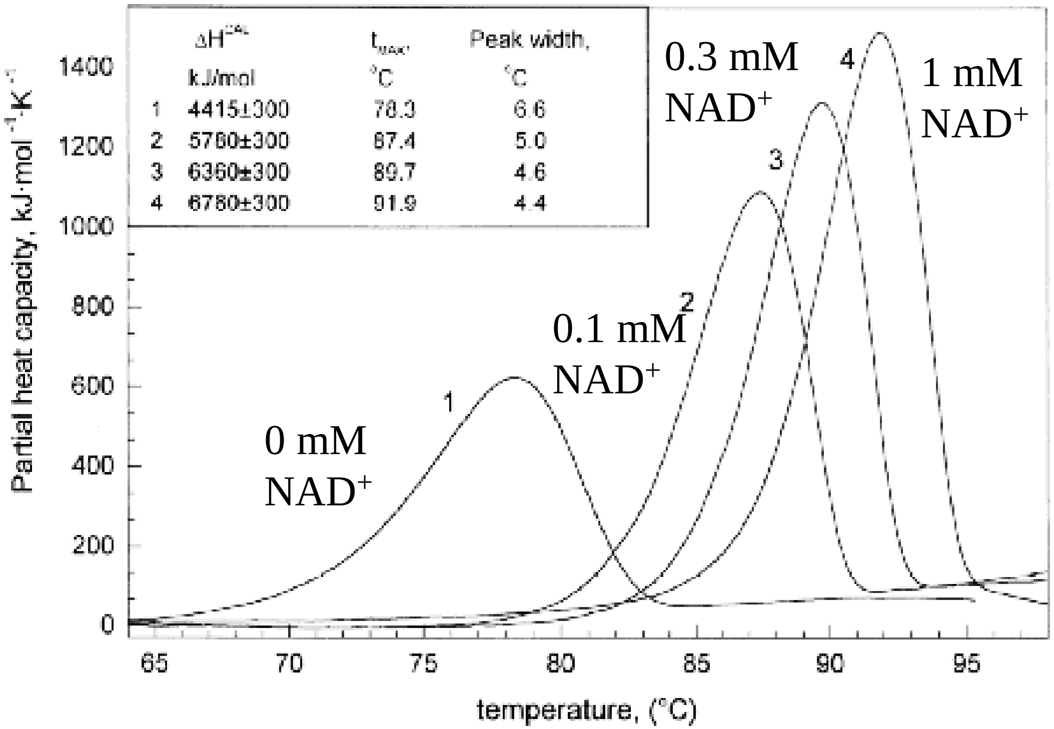
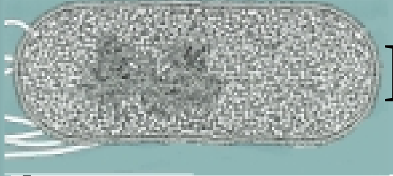


	ΔH^{CAL} kJ/mol	t_{MAX} °C	Peak width, °C
1	4415±300	78.3	6.6
2	5760±300	87.4	5.0
3	6360±300	89.7	4.6
4	6780±300	91.9	4.4

Fig. 2. Temperature dependence of the wild-type apo-*B. stearothermophilus* GAPDH partial heat capacity in the presence of different NAD$^+$ concentrations. The experiments were carried out as described in Fig. 1, at pH 8.0. 1, apoenzyme; 2,3,4, the same as 1, but in the presence of 0.1 mM, 0.3 mM and 1.0 mM NAD$^+$, respectively.



Example 4: Unfolding of lysozyme

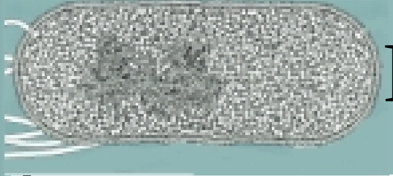
We are given the following data for the denaturation of lysozyme:

	10	25	60	100	°C
ΔG° kJ/mol	67.4	60.7	27.8	-41.4	
ΔH° kJ/mol	137	236	469	732	
ΔS° J/ K mol	297	586	1318	2067	
$T\Delta S^\circ$ kJ/mol	69.9	175	439	771	

Where is the denaturation temperature?

Why does it get *more* endothermic as temperature increases?

What then is special about the temperature at which the denaturation is spontaneous?



Free Energy and Chemical Equilibria

Living organisms depend on sponteous processes to maintain life.

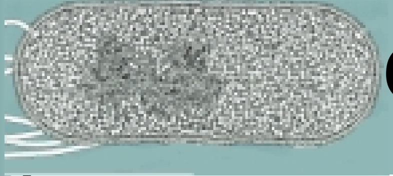
But are all reactions in an organisms spontaneous?

Le Châtelier’s principle gives us some understanding of how the equilibrium of a system changes when we perturb it.

> *"Any change in one of the variables that determines the state of a system in equilibrium causes a shift in the position of equilibrium in a direction that tends to counteract the change in the variable under consideration."*

We are interested in how system try and tend towards equilibrium and what clever tricks are played to keep us out of equilibrium.

The free energy, or more correctly, the ***chemical potential*** is our measure of roughly how far we have to go to come to equilibrium. It is a potential energy of sorts.



Chemical Potential: Part 0

We will use chemical potential to give quantitative meaning to Le Châtelier's principle.

Chemical potential is the ***partial molal Gibbs free energy.***

$$\mu = \overline{G}$$

Thus increasing the concentration of a substance will always increase its chemical potential.

Manipulating concentrations can therefore change the spontaneous direction of reactions.

We are going to break biochemical processes into five sections.

1) metabolism
2) pH reactions
3) oxidation-reduction
4) solvent/ion interactions
5) assembly of multicomponent cellular structures

The biochemical standard state

The standard states in biology are somewhat different than are defined for general chemistry.

As we will see, standard states define when the ***activity*** of a species is equal to 1.

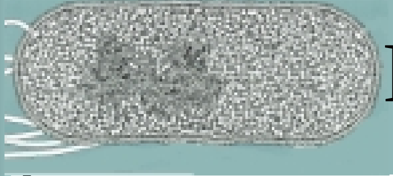
For biochemistry we have

P = 1 atm
pH = 7.0 (as opposed to 0 for chemists)

Temperature is not specified. Generally it is 25 °C rather than 37 °C.

The ***activity*** of a compound is related to its concentration.

In the ideal case it ***is*** the concentration. But when there are real interactions among molecules, the “effective” concentration can be different than the ideal one. This difference is expressed in the ***activity coefficient***.



Free Energy and Equilibrium

An important biological and industrial reaction is the creation of ammonia.

Bacteria fix nitrogen into ammonia for plants to metabolize.
Humans want to “fix” nitrogen in ammonia because it’s a useful reagent.

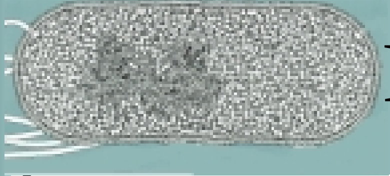
Of course, humans and bacteria will do the process a bit differently.

But all we care about is the overall outcome.

From this we can calculate our thermodynamic state functions.

$$3/2\ H_2(g) \quad + \quad 1/2\ N_2(g) \longrightarrow NH_3(g)$$

To calculate the free energy change we need only the partial pressures, and the temperature



Free Energy and Equilibrium

In order to use the thermodynamic tables to calculate free energy, we have to go to 1 atm.

$$\begin{tikzcd}
\frac{1}{2}N_2(g,P_{N_2})+\frac{3}{2}H_2(g,P_{H_2}) \arrow[r, "\Delta G_T"] \arrow[d, "\Delta G_1"'] & NH_3(g,P_{NH_3}) \\
\frac{1}{2}N_2(g,1atm)+\frac{3}{2}H_2(g,1atm) \arrow[r, "\Delta G_T^\circ"] & NH_3(g,1atm) \arrow[u, "\Delta G_2"']
\end{tikzcd}$$

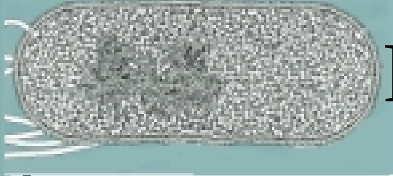
So

$$\Delta G_T = \Delta G_1 + \Delta G^\circ_T + \Delta G_2$$

and we know from before that

$$G(P_2) - G(P_1) = nRT\ln(\frac{P_2}{P_1})$$

$$\Delta G_1 = \frac{1}{2}RT\ln\left(\frac{1}{P_{N_2}}\right) + \frac{3}{2}RT\ln\left(\frac{1}{P_{H_2}}\right), \Delta G_2 = RT\ln\left(\frac{P_{NH_3}}{1}\right)$$



Free Energy and Equilibrium

$$\Delta G_1 = \frac{1}{2} RT \ln\left(\frac{1atm}{P_{N_2}}\right) + \frac{3}{2} RT \ln\left(\frac{1atm}{P_{H_2}}\right), \Delta G_2 = RT \ln\left(\frac{P_{NH_3}}{1atm}\right)$$

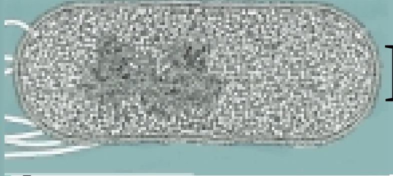
So

$$\Delta G_T = \Delta G_T^\circ + \frac{1}{2} RT \ln\left(\frac{1}{P_{N_2}}\right) + \frac{3}{2} RT \ln\left(\frac{1}{P_{H_2}}\right) + RT \ln\left(\frac{P_{NH_3}}{1}\right)$$

$$= \Delta G_T^\circ + RT \ln\left(\frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}}\right)$$

Which is, getting close to looking like ΔG_T depends on an ***equilibrium quotient.***

$$\Delta G_T = \Delta G_T^\circ + RT \ln(Q)$$



Free energy for chemical reactions

For an arbitary chemical reaction (in gas phase)

$$n_A\,A + n_B\,B + n_C\,C \ldots \xrightarrow{\qquad\qquad} n_\alpha\,\alpha + n_\beta\,\beta + n_\gamma\,\gamma + \ldots$$

we know that

$$\Delta G_{rxn} = \Sigma\, G(\text{products}) - \Sigma\, G(\text{reactants})$$

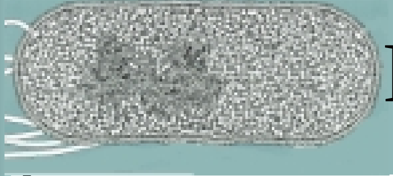
and that

$$\Delta G_{rxn} < 0$$

means the reaction will occur spontaneously (under the specified conditions!)

Calculation of ΔG_{rxn} can be tricky because material in different states may be reacting.

Let’s start by considering gases.



Free energy for chemical reactions

Let’s consider the free energy of pure gas in a reaction whose **initial** and **final** temperatures are the same:

In this case :

$$dG_{rxn} = V\,dP$$

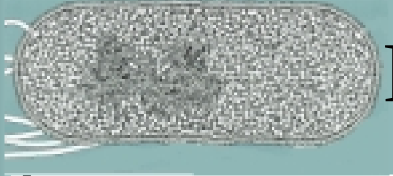
For a reaction involving an ideal gas then:

$$dG_{rxn} = (nRT/P)\,dP = nRT\,d\ln(P)$$

Integrating from a standard state to a new state for gas A gives:

$$G_A = G^\circ_A + nRT\ln(P_A/P^\circ_A)$$

where G°_A is the free energy of formation of the compound from its elements in standard state.



Free energy for chemical reactions

$$G_A = G°_A + nRT \ln(P_A/P°_A)$$

The common standard state for gases is P = 1atm.

So:

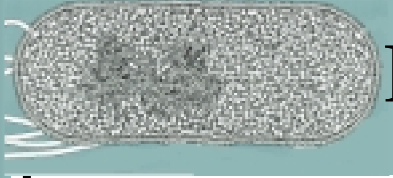
$$G_A = G°_A + nRT \ln(P_A/1\text{ atm})$$
$$G_A = G°_A + nRT (\ln(P_A) - \ln(1\text{ atm}))$$

Note that unless P_A is also in units of atmospheres this equation cannot be evaluated (**you can't take a logarithm of a number with units**)

Assuming that P_A is in atmospheres:

$$G_A = G°_A + nRT (\ln(P_A) - \ln(1)) = G°_A + nRT \ln(P_A)$$

This is for ***one species in a gas phase chemical reaction!***



Free energy for chemical reactions

$$G_A = G°_A + nRT\,(\ln(P_A) - \ln(1)) = G°_A + nRT\ln(P_A)$$

So for multiple species in a reaction like:

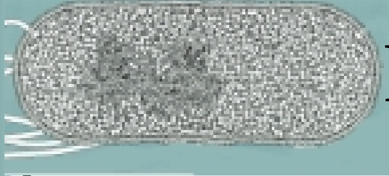
$$n_A\,A + n_B\,B + n_C\,C \ldots \xrightarrow{\hspace{5cm}} n_\alpha\,\alpha + n_\beta\,\beta + n_\gamma\,\gamma + \ldots$$

we get that

$$\begin{aligned}\Delta G_{rxn} &= \Sigma\, G°(\text{products}) - \Sigma\, G°(\text{reactants}) \\ &\quad + \Sigma_{(\text{products})}\, n_i RT\ln(P_i) - \Sigma_{(\text{reactants})}\, n_j RT\ln(P_j)\end{aligned}$$

$$\boxed{\Delta G_{rxn} = \Delta G^\circ + RT\ln\left(\frac{\prod_{i=\text{products}} P_i^{n_i}}{\prod_{j=\text{reactants}} P_j^{n_j}}\right) = \Delta G^\circ + RT\ln(Q)}$$

where Q is the equilibrium quotient. Applies in and out of equilibrium.



Free energy for chemical reactions

Let’s work an example:

$$2\ CO\ (g)\ +\ O_2\ (g) \longrightarrow 2\ CO_2\ (g)$$

The free energy change for this reaction is simply:

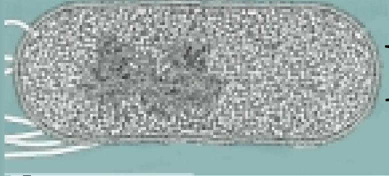
$$\Delta G°_{rxn} = 2\ \Delta G°_{289}(CO_2) - 2\ \Delta G°_{289}(CO) - \Delta G°_{289}(O_2)$$

We can calculate this using numbers from the appendix:

$$\Delta G°_{rxn} = 2\ (-394.36) - 2(\ -137.17) - 0\ \ (kJ/mol) = -514.38\ kJ/mol$$

A relatively large negative number!

So if we have CO (g) at 1 atm and O_2 (g) at 1 atm we have a big tendency to go!



Free energy for chemical reactions

But what if we are not in some standard state? We use:

$$\boxed{\Delta G_{rxn} = \Delta G^{\circ} + RT\ln\left(\frac{\prod\limits_{i=\text{products}} P_i^{n_i}}{\prod\limits_{j=\text{reactants}} P_j^{n_j}}\right) = \Delta G^{\circ} + RT\ln(Q)}$$

Plugging in:

$$\Delta G_{rxn} = \Delta G^{\circ} + RT\ln\left(\frac{P_{CO_2}^2}{P_{CO}^2 P_{O_2}}\right)$$

So if we start with some arbitrary pressures we can calculate the tendency of the reaction to go.

But let’s consider what happens at equilibrium.